

## Impact of acetone on phase boundary of methane and carbon dioxide mixed hydrates

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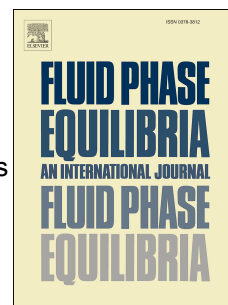
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# Accepted Manuscript

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## **Impact of acetone on phase boundary of methane and carbon dioxide mixed hydrates**

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## Abstract

In this work, the hydrate phase boundary of a gas mixture consisted of 29.9 mol% CH<sub>4</sub> and 70.1 mol% CO<sub>2</sub> is experimentally studied in the presence of 1 to 7 mol% of an aqueous acetone solution. Results indicated that acetone acts as a weak inhibitor on this gas mixture. In addition, enthalpy of hydrate dissociation for this system is reported. Based on the results, the inhibition effect of acetone is found to be decreasing with the increase of acetone concentration while the enthalpy of hydrate dissociation is increasing with the increase of acetone concentration within the studied range.

**Keywords:** Hydrate phase boundary; Acetone; Carbon dioxide-Methane Mixed Gas; Inhibitor; Enthalpy of dissociation

## 1. Introduction

Gas hydrates are crystalline complex structures consist of hydrated polyhedron lattice, which acts as a host and entrapped guest molecules. Guest molecules, generally, may carry strong hydrophobic characteristics and none or weak polarity, which leading to immiscibility with water [1]. Still, some water soluble hydrocarbon can form clathrate hydrate due to minimization of Gibbs free energy of the guest and host molecules at high pressure and relatively low temperatures [2].

Increasing energy demand across the globe in the 21<sup>st</sup> century makes non-conventional fuel resources to become economically interesting. This includes the development of high carbon dioxide (CO<sub>2</sub>) gas reservoir where CO<sub>2</sub> content can be more than 50 mol% of the gas originally in place. For example, K5 field located offshore of Sarawak, Malaysia with 25.65 trillion SCF gas reserve, shows evidence of bearing more than 70 mol% CO<sub>2</sub>. [3] In addition, biogas and landfill gas that can be classified as renewable energy resources, mostly consist of 45 to 60 vol% methane (CH<sub>4</sub>) and 40-60 vol% CO<sub>2</sub> with traces of some other gases [4, 5]. Economically, the high CO<sub>2</sub> gas requires an efficient CO<sub>2</sub> separation module to make these resources marketable or even suitable as feedstock for manufacturing processes [3]. On the other hand, international regulations, such as Kyoto Protocol, emphasize on the reduction of greenhouse gases emission, particularly CO<sub>2</sub>, to the atmosphere [6, 7]. Therefore, both economic and environmental aspects are pointing to a need for a clean CO<sub>2</sub> separation process prior to the utilization of these new resources.

The common gas separation technologies such as chemical absorption, adsorption, cryogenic distillation and membrane separation, are incapable, both economically and technically, to capture the large amounts of CO<sub>2</sub> from gas streams. Some critical problems are associated with large energy consumption, corrosion, foaming, and low capacity. For example, estimations showed that the deployment of absorption capturing technology in flue gas cleaning from a modern power plant can reduce the thermal efficiency from approximately 45% to approximately 35%. [8]. Therefore,

development of new and existing capturing technologies should lower the energy requirements in order to minimize the overall costs as well as environmental impacts [9].

Utilization of gas hydrate as a separation technology is one of the alternatives. Separation of  $\text{CO}_2$  from  $\text{N}_2$  by forming gas hydrate in the presence of tetrahydrofuran (THF) was reported by Kang and Lee [10]. According to their investigation, utilization of hydrate technology is less energy intensive compared to common capturing process due to the moderate temperature condition of 273 to 283 K. In addition, using THF can decrease hydrate formation pressure and consequently decrease the overall energy consumption for the process [10]. There are several publications in the open literature that suggest hydrate formation process for separation of  $\text{CO}_2$  from  $\text{N}_2$ ,  $\text{H}_2$  and some other gases. Eslamimanesh et al. (2012) presented a comprehensive survey of experimental studies dealing with separation of a gases by hydrate formation technology [11]. However, separation of  $\text{CO}_2$  from  $\text{CH}_4$  received less attention in these studies. Seo et al. at (2000) showed that separation of  $\text{CO}_2$  from  $\text{CH}_4$  is possible through hydrate formation process [12]. Both  $\text{CO}_2$  and  $\text{CH}_4$  are good gas hydrate former and their gas hydrate phase boundaries are relatively close to each other. This makes their separation through hydrate formation process more challenging. A suitable promoter to enhance the separation may be the key. THF as the most famous promoter is shown good promotion effects for both gases [13, 14]. Consequently, it cannot be a good candidate to enhance their separation.

Acetone, as a common solvent, can be a good candidate for this purpose. Acetone has shown a thermodynamic promotion effect on methane hydrate formation at low concentration [14, 15]. The promotion effects of acetone on methane hydrate is first observed by Ng and Robinson when they were looking for a new inhibitor for methane hydrate [16]. Acetone is a polar compound that is liquid at room temperature. At first glance, acetone seems to be an inhibitor, as it has many characteristics in common with alcohols. But, at low concentrations, it thermodynamically promotes the methane hydrate formation condition. The maximum promotion effect was observed at around 6 mol% concentration [17]. This promotion effect is converted to inhibition when acetone concentration is higher than 30 mol% [15]. On the other hand, acetone showed thermodynamic inhibition effect for carbon dioxide hydrate at all concentration [18]. Therefore, as acetone has different effects on pure  $\text{CH}_4$  and  $\text{CO}_2$  hydrates at low concentrations, it may show some selectivity on separation of these gases by hydrate formation process. Yet, prior to study the separation efficiency, the equilibrium phase boundary for such system should be studied and analyzed first. Acetone and water are well known for non-ideal behaviors and hence predictions of hydrate formation in such system through thermodynamic modeling have a considerable error. Thus, in this work, the phase boundary of gas hydrate for a system of water + acetone +  $\text{CO}_2$  +  $\text{CH}_4$  is experimentally measured and reported.

102

## 103 2. Experimental Section

### 104 2.1. Material

105 Acetone with purity of 99.8% was purchased from Merck Millipore. A pre-mixed CH<sub>4</sub> and CO<sub>2</sub>  
106 gas mixture was purchased from AirProduct Singapore Pte. Ltd. The gas mixture ratio as specified by  
107 the supplier is 29.99 mole % CH<sub>4</sub> and 70.01 mol% CO<sub>2</sub>. This CO<sub>2</sub> to CH<sub>4</sub> ratio is selected in order to  
108 simulate the K5 field gas composition and the pre-mixed gas was used without any further  
109 purification. Deionized water was used to prepare aqueous acetone solutions.

110

### 111 2.2. Apparatus

112 A high-pressure cell, manufactured by Dixon FA engineering Sdn. Bhd is used for the  
113 measurement of gas hydrate phase boundary. The schematic of the experimental rig is depicted in  
114 Figure 1. The equilibrium cell is made of stainless still and has an internal volume of 500 ml. The cell  
115 is equipped with a PT-100 platinum thermometer with the accuracy of  $\pm 0.15$  °C. A GP-M250  
116 Keyence pressure transducer with the accuracy of  $\pm 1.0\%$  full span is used to measure the pressure  
117 inside the cell. In addition, a magnetic stirring system consisted of a 2-bladed pitch impeller and a 400  
118 rpm motor is used to agitate liquid in the cell. The cell is immersed inside a thermostatic bath. The  
119 bath temperature is controlling by a PID controller with an accuracy of  $\pm 0.3$  °C. In addition, the bath  
120 temperature set point is programmable through data acquisition system. Pressure and temperature  
121 data is recorded every second.

122

### 122 INSERT FIGURE 1

123 **Figure 1.** Simplified schematic of experimental rig.

124

### 125 2.3. Procedure

126 The -hydrate equilibrium points were measured by employing an isochoric method. The cell was  
127 washed using distilled water and dried. The extra air was removed from the cell using a vacuum  
128 pump. 100 cm<sup>3</sup> of aqueous acetone solution at the desired concentration was fed into the cell through  
129 liquid injection point and gas was purged three times to ensure complete removal of air from the  
130 system. Then, gas was introduced to the cell until the desired pressure is achieved at room  
131 temperature. The stirring system was turned on and then the temperature was decreased to 273 K.  
132 System was kept at this temperature for 4 hrs to ensure gas hydrate formation. After that, the system  
133 was warmed stepwise to 293 K. At each step, the temperature was held constant for 30 min to 240  
134 min, according to the set point temperature and expected equilibrium temperature. The hydrate  
135 dissociation condition was determined through P-T diagram, as described by Tohidi et al.[19].

To produce the phase boundary for  $\text{CO}_2 + \text{CH}_4 + \text{water} + \text{acetone}$  system, four different acetone concentrations was studied at three different pressures. In addition, to validate the accuracy of the experimental setup, methane hydrate phase boundary in the presence of deionized water at three different pressures was measured and compared with literature data.

### 3. Results and Discussion

#### 3.1. Validation of the new setup

The pressure-temperature profile for  $\text{CH}_4$ -water system as a sample of the experimental procedure followed in this work is depicted in Figure 2. The cooling step is set to be fast to shorten the experimental time. The rapid pressure drop is due to the hydrate formation. The heating part consisted of a fast heating step following by several slow steps. The location of the change in the P-T slope, as shown in Figure 2, is taken as the hydrate equilibrium point. The methane hydrate equilibrium point shown in Figure 2 is 5.808 MPa and 281.35 K. In Figure 3,  $\text{CH}_4$ -water equilibrium data points are included. As shown in this figure, the measured data coincides with pure methane hydrate data reported by Nakamura et al. [20].

#### INSERT FIGURE 2

**Figure 2.** Pressure-Temperature profile measured during  $\text{CH}_4 + \text{water}$  experiment.

#### 3.2. $\text{CH}_4 + \text{CO}_2 + \text{acetone} + \text{water}$ hydrates Equilibrium data

The equilibrium points of  $\text{CH}_4 + \text{CO}_2 + \text{acetone} + \text{water}$  hydrates are tabulated in Table 1. Four different aqueous solutions of 1, 3, 5 and 7 mol% of acetone are studied in this work. In addition, blank deionized water is studied as reference condition. For each solution, the hydrate dissociation condition is reported for three to four different pressures between 2.68 to 5.36 MPa. In each experiment, the pre-mixed gas mixture of 29.9 mol%  $\text{CH}_4$  and 70.1 mol%  $\text{CO}_2$  is used as the feed gas. In each experiment, based on starting pressure and temperature condition the final concentration of gas and liquid phase composition is changed. In Table 1, the  $\text{CO}_2$  and  $\text{CH}_4$  concentration in gas phase is calculated by vapor-liquid equilibrium (VLE) calculations at equilibrium pressure and temperature with utilization of a  $\phi$ - $\phi$  approach, using Peng-Robinson equation of state [21] with modified Huron-Vidal (MHV1) mixing rule [22] and UNIFAC activity coefficient model [23] to calculate the non-ideality of system.

As previously mentioned, the presence of acetone promotes  $\text{CH}_4$  hydrate formation at concentrations lower than 7 mol%, while for  $\text{CO}_2$  hydrate it acts as an inhibitor at all concentrations. Therefore, for a mixture of  $\text{CO}_2$  and  $\text{CH}_4$ , its impact is more complicated. The gas hydrate phase boundaries of  $\text{CH}_4$ ,  $\text{CO}_2$  and mixed  $\text{CO}_2/\text{CH}_4$  in the presence of 1 mol% acetone aqueous solution is

depicted in Figure 3. The data for CH<sub>4</sub> + acetone in Figure 3 to 6 are taken from Seo et al. [14] and Partoon et al. [15] while those for CO<sub>2</sub> + acetone data are taken from Maekawa work [18]. In addition, HLV equilibrium data of CH<sub>4</sub> hydrate and CO<sub>2</sub> hydrate in pure water are also illustrated in Figure 3 to provide better observation of acetone impact on gas hydrate phase boundary. The CH<sub>4</sub> and CO<sub>2</sub> hydrate data are taken from Nakamura et al. [20] and Sabil et al. [24], respectively.

**Table 1.** Gas hydrate equilibrium condition for CO<sub>2</sub> + CH<sub>4</sub> + acetone + water system. The feed gas consisted of 29.9 mol% CH<sub>4</sub> and 70.1 mol% CO<sub>2</sub>.

Acetone concentration in solution (mol%)	Equilibrium condition				Acetone concentration in solution (mol%)	Equilibrium condition			
	y <sup>1</sup> CO <sub>2</sub> (mol%)	y <sup>1</sup> CH <sub>4</sub> (mol%)	T <sup>2</sup> (K)	P <sup>2</sup> (MPa)		yCO <sub>2</sub> (mol%)	yCH <sub>4</sub> (mol%)	T (K)	P (MPa)
0	69.95	34.16	281.35	3.25	3	63.66	35.84	281.65	4.17
	69.97	33.36	283.05	4.35		64.13	35.22	282.85	5.13
	69.98	32.75	284.65	5.32		64.92	34.37	283.15	5.36
1	64.84	34.95	279.35	3.22	5	60.70	38.77	280.65	3.32
	65.54	34.22	281.1	4.16		61.84	37.54	282.05	4.18
	66.31	33.35	282.85	5.28		62.74	36.48	282.95	5.05
3	62.16	37.44	279.25	2.68	7	57.83	41.57	281.2	3.36
	62.78	36.81	279.85	3.19		59.48	39.85	282.25	4.22
	63.02	36.54	280.75	3.71		60.65	38.52	283.35	5.03

<sup>1</sup> Calculated value

<sup>2</sup> Standard combined uncertainties:  $u_c(P) = 0.07$  MPa and  $u_c(T) = 0.1$  K.

### INSERT FIGURE 3

**Figure 3.** HLV phase boundary of CH<sub>4</sub>, CO<sub>2</sub> and their mixture in the presence of 1 mol% acetone solution.

As shown in Figure 3, the presence of 1 mol% acetone in the solution shifts CO<sub>2</sub> hydrate phase boundary to lower temperature, while it moves CH<sub>4</sub> phase boundary to the higher temperature condition. This resulted in almost the same equilibrium hydrate boundary for CO<sub>2</sub>, CH<sub>4</sub> and consequently their mixture, as it shown in this figure. By increasing acetone concentration to 3 mol%, its promotional effect on CH<sub>4</sub> hydrate and its inhibition effect on CO<sub>2</sub> hydrate is increasing and thus creating a distinct separation between the two equilibrium lines as depicted in Figure 4.

### INSERT FIGURE 4

**Figure 4.** HLV phase boundary of CH<sub>4</sub>, CO<sub>2</sub> and their mixture in the presence of 3 mol% acetone solution.

As shown in Figure 4, methane hydrate phase boundary is shifting to a higher temperature in the presence of 3 mol% acetone. In contrast, the inhibition effect of acetone significantly reduced the



phase boundary of CO<sub>2</sub> hydrate. Therefore, in the presence of 3 mol% of acetone in the aqueous solution, CH<sub>4</sub> hydrate is forming at higher pressure and temperature than that of CO<sub>2</sub> hydrate. For the mixed gas, as expected, the hydrate phase boundary is laying between that of pure gases hydrate-liquid-vapor (HLV) equilibrium line. However, as the studied gas mixture is rich in CO<sub>2</sub>, its HLV line is tending toward CO<sub>2</sub> HLV line.

## INSERT FIGURE 5

**Figure 5.** HLV phase boundary of CH<sub>4</sub>, CO<sub>2</sub> and their mixture in the presence of 5 mol% acetone solution.

A similar trend is observed for a system with 5 mol% aqueous acetone solution as depicted in Figure 5. Due to the increase in acetone concentration, the gap between methane and carbon dioxide hydrate phase boundaries is increasing. This behavior can be attributed to cage occupancy competition. First of all, because of acetone molecular size, the presence of acetone in the system converts structure sI methane and carbon dioxide hydrate to structure sII, where acetone molecules are occupying the large cavities of structure sII hydrates. For methane hydrate, sII provides lots of small cages where methane molecules can best fit inside. In contrast, due to the diameter of CO<sub>2</sub> molecules, the small cages are very tight and although CO<sub>2</sub> molecules can also occupy small cages of both sI and sII, they tend to go into large cavities [1]. This creates a competition between CO<sub>2</sub> and acetone molecules to occupy the larger cavities of sII hydrates. Therefore, for methane hydrate at low concentrations, where acetone molecules occupy the large cavities and methane occupies mostly small cavities, acetone promotes the hydrate formation condition while the similar trend is not observed for the CO<sub>2</sub> system. It is interesting to notice that the maximum promotion effect of acetone in such system is at 6 mol% where they can completely fill all large cavities of sII hydrate. At higher concentrations, the polar properties of free acetone molecules start to inhibit the hydrate formation. Thus, at 30 mol% acetone becomes inhibitor for CH<sub>4</sub> hydrate [15, 17]. For CO<sub>2</sub> hydrates, the competition between acetone and CO<sub>2</sub> molecules along with polar properties of both compounds convert acetone to an inhibitor at all concentrations.

## INSERT FIGURE 6

**Figure 6.** HLV phase boundary of CH<sub>4</sub>, CO<sub>2</sub> and their mixture in the presence of 7 mol% acetone solution.

Figure 6 depicts CH<sub>4</sub>, CO<sub>2</sub> and CO<sub>2</sub>-CH<sub>4</sub> mixture phase boundaries in the presence of 7 mol% of acetone. At this concentration, the promotion effect of acetone on methane hydrate phase boundary is started to decrease. This is, however, not directly affected the phase boundary of the CO<sub>2</sub>/CH<sub>4</sub> system.

The impact of acetone on mixed gas hydrate HLV is inhibition for all acetone concentrations. Figure 7 compares the gas hydrate equilibrium temperature of the mixed gas as a function of acetone concentration at different pressures. As it shown in this figure, the presence of acetone in the solution

decreases the mixed gas hydrate equilibrium temperature at constant pressure. This thermodynamic inhibition effect is a weak function of acetone concentration. For example, at 5 MPa and 1 mol% of acetone the hydrate equilibrium temperature is decreased around 2 K. This shift in equilibrium temperature is 1.4 K at 7 mol% for the same pressure.

### INSERT FIGURE 7

**Figure 7.** The impact of acetone on mixed gas hydrates equilibrium temperature at constant pressures.

### 3.3. Enthalpy of dissociation

Another important parameter for industrial application of gas hydrate is enthalpy of dissociation,  $\Delta H_d$ , which by definition is the amount of heat required for dissociating hydrate crystals to liquid and gas phases. Gas hydrate enthalpy of dissociation is quantitatively much higher than water enthalpy of melting.  $\Delta H_d$  is equal to the amount of heat being released during hydrate formation and it is known as enthalpy of hydrate formation. This parameter plays essential roles in process design and optimization. To calculate  $\Delta H_d$ , Clausius–Clapeyron type equation can be applied:

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta H_d}{zR} \quad (1)$$

where,  $P$  and  $T$  are equilibrium pressure and temperature,  $z$  is gas compressibility and  $R$  is universal gas constant [1]. The values for  $\Delta H_d$  of the studied system are reported in Table 2. At equilibrium condition, it can be assumed that amount of hydrate phase is negligible and therefore, the system mainly consisted of liquid and gas phase. However, the studied system is considerably non-ideal in liquid phase because of acetone's presence. Therefore, to calculate the gas compressibility, vapor-liquid equilibrium (VLE) of system at equilibrium pressure and temperature is calculated by a  $\phi$ - $\phi$  approach, using Peng-Robinson equation of state [21] with modified Huron-Vidal (MHV1) mixing rule [22] and UNIFAC activity coefficient model [23] to calculate the non-ideality of system.

**Table 2.** Average enthalpy of dissociation for studied systems.

Acetone concentration in solution (mol%)	$\Delta H_d$ (kJ/mol)
0	55.6
1	69.0
3	90.7
5	92.2
7	94.5

As presented in this table, the  $\Delta H_d$  in the absence of acetone is in the range of sI hydrates value such as methane and carbon dioxide [25, 26].  $\Delta H_d$  is increasing as a result of large cage occupation by acetone molecules. However, the values are less than common sII hydrate formers such as propane ( $\Delta H_d = 129$  kJ/mol) [1]. This is shown that both small and large cavities of sII hydrate are filling with

gases. In addition, increasing the enthalpy of dissociation with acetone concentration indicates that acetone is occupying large cavities of sII crystals more than CO<sub>2</sub> or even CH<sub>4</sub>. This result is in line with the impact of acetone on HLV of studied system, as discussed before.

#### 4. Conclusion

The phase boundary of CO<sub>2</sub> and CH<sub>4</sub> gas mixture in the presence of acetone solution is experimentally measured in this work. The results indicated that presence of acetone in the solution has inhibition effects on mixed gas HLV phase boundary. However, this inhibition effects is decreasing by increasing the acetone concentration in the studied range. In addition, the enthalpy of dissociation for this system is presented in this work. Enthalpy analysis indicates that chance of acetone for the occupation of large cavities of sII hydrate is increasing by an increase in acetone concentration. These findings show that acetone has the potential to act as a selective additive for separation of CO<sub>2</sub> and CH<sub>4</sub>. The slight inhibition effect of acetone on the equilibrium condition does not have a large impact on the operational condition of any proposed process for separation of these gases. In such process, at a certain pressure, the operating temperature should be put well below the equilibrium temperature to provide enough super-saturation. As a matter of fact, the reduction of water freezing point as a result of acetone presence in the system can give this opportunity to reduce the operational temperature to below ice point temperature. However, further study is required to investigate this application for acetone. Especially, the amount and composition of captured gas by hydrate at a certain temperature below the hydrate equilibrium temperature should be measured to find out if acetone can work as a selective additive for separation of CO<sub>2</sub> from CH<sub>4</sub> or not

#### Acknowledgements

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**Figure 8.** Simplified schematic of experimental rig.

**Figure 9.** Pressure-Temperature profile measured during CH<sub>4</sub> + water experiment.

**Figure 10.** HLV phase boundary of CH<sub>4</sub>, CO<sub>2</sub> and their mixture in the presence of 1 mol% acetone solution.

**Figure 11.** HLV phase boundary of CH<sub>4</sub>, CO<sub>2</sub> and their mixture in the presence of 3 mol% acetone solution.

**Figure 12.** HLV phase boundary of CH<sub>4</sub>, CO<sub>2</sub> and their mixture in the presence of 5 mol% acetone solution.

**Figure 13.** HLV phase boundary of CH<sub>4</sub>, CO<sub>2</sub> and their mixture in the presence of 7 mol% acetone solution.

**Figure 14.** The impact of acetone on mixed gas hydrates equilibrium temperature at constant pressures.

AB: Alcoholic Bath  
 A/D: Analog to Digital module  
 C: High pressure cell  
 D: Data logging program  
 G: Gas Cylinder  
 GB: Gas Booster  
 LV: Liquid Valve  
 M: Magnetic Motor  
 PSV: Pressure Safety Valve  
 PT: Pressure Transmitter  
 PT-100: Temperature sensor  
 TCS: Temperature control system  
 TT: Temperature Transmitter  
 VP: Vacuum Pump

